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THE SYNTHESIS AND CHARACTERIZATION OF SINTERED AND HOT-PRESSED SODIUM ZIRPSIOS

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by

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ABSTRACT

Recent work in CANMET has questioned the claim made by others that stable solid electrolytes can be produced in the system of sodium-zirconium-phosphorus-silicon oxides. The present work demonstrates that, even with highly reactive gel-processed raw materials, a glass phase is always produced under conventional sintering conditions and it is suggested that this phase is responsible for the progressive degradation of these materials in the presence of water.

Through the use of a powder hot-pressing process, dense sintered samples were also produced at temperatures 50 - 225 K lower and under conditions that suppressed the loss of volatile components. However, although the loss of phosphorus and sodium from the compacts was reduced, the product was still degraded by water.

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INTRODUCTION

With the constantly increasing emphasis being placed on the efficient use of energy today, greater attention is being paid to many electrochemical devices such as advanced batteries and fuel cells as they offer the opportunity for transforming energy from one form to another without suffering the considerable Carnot-cycle losses that are incurred in all heat engines. This interest was triggered by the excellent pioneering work of researchers at the Ford Motor Co., Dearborn, who were the first to show the considerable ionic conductivity of sodium beta-alumina and how it may be exploited in a Na-S battery that is now known as the 'beta-battery'. Following the action of the OPEC countries in 1973 in markedly increasing the cost of crude oil, this interest was given a further boost and, as a result, a considerable number of research groups began studying a very wide range of solid electrolytes in the mid 1970's.

One of the undesirable features of beta-alumina arises from its highly anisotropic structure and the 2D conduction that results. In a randomly oriented, polycrystalline body this leads to the formation of 'blocking' boundaries in which the fast-conducting basal plane of one grain will lie normal to that of its neighbour. This results in a lower conductivity and hence a lower level that can be obtained from any device. If a 3D conductor were used, this restriction would not apply and a higher power level could be attained. It is for this reason that a considerable effort has been under way in various laboratories to identify those 3D conductors that otherwise have similar properties to those of the beta-aluminas.

One such group of materials occurs in the quaternary oxide system of sodium, zirconium, phosphorus and silicon and was first identified in the U.S.A. in 1976 (1,2). Since then, a related group of materials has also been identified in the same system by researchers in Germany (3). As an added appeal, these compositions can be fabricated at significantly lower temperatures than the beta"-aluminas. Thus they are potentially ideal candidate materials for use in all applications presently envisaged for the two-dimensionally (2D) conductive beta"-aluminas (such as the Na-S battery) and they are under study in a number of laboratories.

Unfortunately, recent CANMET work has shown that a glass phase is commonly formed during the sintering of these materials and it is suggested that the presence of this phase, irrespective of composition, is responsible for their lack of durability. Consequently, the present work was undertaken to determine if the conditions of sintering influenced the nature of the product, particularly its stability to water. Additionally, it was thought that the use of hot pressing at a temperature lower than that required for sintering would not only suppress the loss of phosphorus and, to a lesser extent, sodium from the system during heating but might also eliminate the formation of glass entirely, resulting in a more durable material.

EXPERIMENTAL PROCEDURE

The raw materials were synthesised by a wet chemical method so that homogeneous, highly reactive material would be exploited that would minimize the time required at elevated temperature to sinter the pressed bodies to high density. In practice, maximum sintering times of 30 min were employed in this work, compared with up to 12-h sintering cycles necessary for ball-milled material used by researchers elsewhere (1,3), thereby minimizing the loss of volatile material from the system.

Raw Materials Synthesis

Table 1 gives the two series of compositions studied in this work. For convenience, the first series is referred to as Hong material and the other as Max Planck material, in each of which the value of x ranges from 1.5 - 2.2.

The details for synthesising materials in this system have been given elsewhere (4). Essentially, a solution of sodium formate and ammonium dihydrogen phosphate is mixed with rapid stirring at controlled pH with a freshly prepared silica sol and a finely precipitated suspension of zirconyl hydroxide. The conditions are chosen to retain a fluid system and avoid gelation that probably would lead to phase separation during the drying stage. The mixture is dried to approximately 50% moisture content using a rotary flash evaporator operated between 310 and 315 K at 2.6 kPa. The dried, putty-like material is then dispersed in anhydrous isopropanol and the azeotrope formed is removed in the evaporator to yield a very fine, soft powder. The

use of the alcohol drying stage is found necessary to avoid the formation of very hard granules of dried gel that form if drying is taken to completion in the first stage: such material cannot be sintered without extensive milling (which introduces undesirable contamination). The dried powder is calcined in air for 1 h at 1023 K to decompose some of the components and remove the volatiles prior to use.

Sintering of Samples

Small samples were first formed by uniaxially dry pressing ~0.5 g of material in a 1.27 cm diameter steel die using a pressure of 140 MPa; the bulk density of these green-pressed discs was determined by weighing and measuring their geometrical dimensions. The samples were fast fired in air to minimize the loss of phosphorus- and sodium-containing species. Each sample was placed on a sheet of Pt foil on the hearth of a vertically loading electrically heated muffle furnace capable of heating from room temperature to 1923 K in 10 min. The samples were introduced to the cold furnace and the time of sintering was taken between the time when the temperature reached 5 K below the set-point (as indicated by a thermocouple located close to the sample) and removal of the specimen from the hot zone of the furnace. Four samples were placed on the Pt foil and sintered at the same time - no attempts were made to minimize losses from the upper face by stacking these samples. The sintering temperature was chosen from a series of trial runs to establish the minimum temperature that, in 15 min, would give over 95% relative density.

Hot Pressing of Samples

Samples of each composition were also sintered by hot pressing 6.5-g samples of calcined powder in a graphite die and plunger assembly. To minimize contact of the samples with the graphite furniture, the material was pressed between thin sheets of Pt foil, the backs of which were coated with BN to avoid sticking to the carbon plungers. The pressed samples typically had a diameter of 2.8 cm and a thickness of 5 mm.

As the hot press is insulated with carbon wool of high surface area on which moisture and other materials are adsorbed, the equipment is first out-gassed prior to heating to high temperature. For this purpose, a moderate pressure is maintained on the sample (7 MPa) while the furnace chamber is first pumped down to 0.013 Pa (10^{-4} torr) and heated to ~900 K. When the

chamber pressure starts to drop further, the vacuum is broken by introducing dry argon into the chamber to an absolute pressure of ~90 kPa. At this point, the full pressure is applied to the sample (35 MPa) while it is heated to the pressing temperature. In all cases, the samples were hot pressed for 30 min. After pressing, the pressure was released and the samples allowed to cool in the die to ~400 K prior to opening the chamber and extracting the sample from the die.

Sample Leaching

For these studies, the as-sintered samples were suspended in a known volume (150 mL) of distilled water that was constantly stirred and maintained at a fixed temperature (within 0.1 K) while the pH was monitored with time. To obtain kinetic data, three samples of the same composition were examined at different temperatures.

As the surface area of the air-sintered samples was ~2.5 cm^2, the larger hot-pressed discs were cut and machined to a rectangular shape having the same surface area. To avoid any influence of possible surface contamination, all six sides were diamond machined using isopropanol as the coolant prior to leaching. In practice, four such samples could be obtained from each hot-pressed disc. Because of the major differences that were found in the leaching rate as a function of composition, some of the samples were leached for a maximum of 8 h. In those cases of extreme susceptibility to water ($x > 2$), where it was necessary to take pH readings every 30 sec in the initial stages, much shorter overall leaching times were required.

Microstructural Characterization

All samples were characterized by both optical and scanning electron microscopic examination of polished sections using standard techniques. Quantitative microprobe analysis was carried out on polished sections of the various materials. In selected cases where the glassy phase in the material was thick enough (at least 2 μm), separate analyses of the crystalline and glassy phase were made.

X-ray Diffraction Analysis

All the materials were subjected to X-ray diffraction analysis using a Philips X-ray diffractometer with cobalt Kα radiation. This identified the Na-zirpsio and other crystalline phases such as zirconia, if any, in the materials.

RESULTS

Synthesis and Characterization of Precursor Powders

In Table 2 are listed various compositions of the Hong and Max Planck type materials that were prepared. Obviously, the Max Planck version of the Na-zirpsio is a zirconia deficient form of the Hong Na-zirpsio.

An X-ray diffraction analysis of the powders after drying from the alcohol slurry revealed that most of them were amorphous. However a few of them, especially the Max Planck type, showed the presence of small amounts of crystalline sodium formate especially when $x > 2.0$. Nevertheless, calcination at temperatures over 973 K decomposed all the formates. The major phase detected after calcination at 973 K is cubic/tetragonal zirconia in an extremely finely divided state, Fig. 1. The remaining phases are mostly amorphous.

Each composition was calcined for 1 h at a temperature chosen judiciously to develop maximum density after sintering. The various optimum temperatures used for the different compositions are listed in Table 3.

Sintering of Samples

The optimum sintering temperature for each composition was determined by studying the densification of the compositions as a function of temperature for a constant time of 15 min. Figure 2 represents typical sintering curves for Hong and Max Planck compositions at $x = 1.5$. At this x value, the Max Planck Na-zirpsio is sintered at 1398 K, whereas 1573 K is required for the corresponding Hong composition. At $x = 2.2$, on the other hand, the order of sintering temperature is reversed, as seen from Fig. 3. The optimum temperatures for sintering of the various compositions are also listed in Table 3.

The optimum sintering time was also determined at the optimum temperature selected. Figure 4 illustrates the effect of sintering time on the densification process. A soak time of 15 min was found ideal for all compositions.

Hot Pressing of Samples

The materials could be hot pressed to high density at a temperature considerably lower than that used for the sintering. The densities of the hot pressed materials were also generally greater than those of the corresponding sintered compositions. The various hot pressing temperatures used for the different specimens are also included in Table 3.

Sample Leaching: Reaction With Water

All the samples, whether sintered or hot pressed, react with water to varying degrees. As a result of this reaction, the pH of the water increases with time. The rate of change of pH gives a measure of the reaction kinetics of the particular specimen and hence its stability in water. Using the measured pH values, the hydroxyl ion concentrations of the water extract at various time intervals were calculated using the equations:

$$pH = 14 - pOH \text{ and } pOH = -\log (\text{Hydroxyl ion conc})$$

Reaction Kinetics

Plots of the hydroxyl ion concentration versus time for the various reactions showed three apparently different types of behaviour, as shown in Fig. 5, 6, and 7. In the first case, the kinetics are linear; in the second, initially the rate is linear, but shifts to an almost parabolic rate towards the latter part of the reaction. In the last case, the reaction starts out to be similar to the second case, but eventually the rate drops and reverses. This peculiar behaviour indicates that the reaction of Na-zirpsios with water is a very complex process.

It is speculated that there are at least two parallel competing and/or consecutive reactions occurring in the system. One of these reactions may be an ion exchange of the sodium by the hydronium ions in the water. This reaction may be considered as the hydrolysis of the Na-zirpsio, as the Na-zirpsio can be assumed to be the salt of a strong base and a weak acid. One would expect the hydrolysis reaction to be a phase boundary controlled reaction and hence linear until the final equilibrium conditions are approached. But it cannot show a decrease of pH with time. The fact that the measured pH drops eventually with time in some instances suggests that there is at least another reaction that causes the consumption of the alkali produced by the

hydrolytic ion exchange reactions. This alkali-consuming reaction may be the attack on the Na-zirpsio itself by the alkali produced in the initial reaction. It has been reported that Na-zirpsios are attacked by alkalies at a pH of about 9.3 (5). Thus the drop in pH will occur only if the other reaction which produces the alkali, proceeds until a high pH in the order of 9.3 is reached in the system. Actually, the drop in pH has been observed only in cases where the pH increased to about 9.6.

It is therefore reasonable to assume that the initial linear rate of reaction represents the actual overall reaction rate for the interaction between Na-zirpsio and water. Also, the linear rate constants derived from the initial stage of the reaction should suffice for comparing the reactivities of the various Na-zirpsio compositions under different conditions. Hence linear rate constants utilizing only the initial linear part of the reaction were calculated. This was done by means of a HP 9845 computer program that processed the pH and time inputs into the required parameters and plotted the data linearly and calculated the linear rate constants from the initial slopes of the various lines.

The linear rate constants calculated for the various Na-zirpsios at 298, 303 and 308 K are listed in Table 4. This table shows clearly that the reaction rate increases with an increase of x, irrespective of whether the material is of the Hong type or the Max Planck type, hot pressed or sintered. The Max Planck type materials are generally more reactive than the Hong type and the hot-pressed products are also more reactive than the sintered samples. At low x values the reaction rate increases with an increase of temperature from 298 to 308 K, although at high x values the apparent reaction rate decreases with temperature in several cases.

The activation energies for the reaction of the various compositions both sintered and hot pressed, calculated from the linear rate constants at 298, 303 and 308 K are listed in Table 5. At $x = 1.5$ both the sintered Hong and Max Planck materials show an activation energy of about 20 kcal/mol. It is interesting that several other compositions also give similar activation energy values. The negative activation energies obtained for the Na-zirpsios at high x values may explain the highly unstable nature of these materials. Spontaneous deterioration of Na-zirpsios with high x has been observed in this laboratory and elsewhere.

Microstructure of the Various Products

Typical scanning electron micrographs of polished sections of some of the various compositions are shown in Fig. 8. In the sintered Hong-type compositions, with x values of 1.5 to 2.0, three phases are observed: a light phase, which is zirconia; a grey phase, which is the crystalline Na-zirpsio; and a dark grey phase which appears to be glassy. At x = 2.1 and 2.2 (Hong) the light zirconia phase is almost absent, but the dark grey glassy phase still persists with the lighter grey Na-zirpsio. The absence of zirconia at x = 2.1 and 2.2 is attributed to the low sintering temperature of 1398 K at which these compositions could be fabricated, which eliminated any substantial soda loss from the system. The microstructures of the hot-pressed compositions are extremely fine; free zirconia is virtually absent in all these samples; the glassy phase, if any, is too fine to resolve.

In the Max Planck type materials, no free zirconia is present in any of the compositions, whether prepared by sintering or hot pressing. The sintered samples reveal the presence of the dark grey glassy phase but, due to the fineness of the microstructure, the presence of this phase in the hot-pressed specimens cannot be established. Transmission electron microscopy of these samples is expected to resolve the extremely fine microstructures of these materials.

X-ray Diffraction Analysis

Typical X-ray diffraction charts of a few of the Na-zirpsios are shown in Fig. 9. The major component of all the compositions is Na-zirpsio in the tetragonal or monoclinic form. Small amounts of monoclinic zirconia are observed only in some of the sintered Hong-type products that were prepared at the highest temperatures - of the order of 1573 K and higher. This free zirconia must have resulted from the decomposition of the Na-zirpsio through sodium loss. The fact that no additional phases other than Na-zirpsio and monoclinic zirconia are detected in the system suggests that the third, dark grey phase observed by scanning electron microscopy is glassy in nature.

DISCUSSION OF RESULTS

Na-zirpsios as Solid Solutions

It has been suggested that the Hong Na-zirpsios are not true solid solutions between the anticipated end-members because of the presence of free monoclinic zirconia in the sintered products (3). However, this argument does not prove that they are not true solid solutions. In fact, the Hong Na-zirpsios formed at temperatures about 1373 K from highly reactive precursor powders do not contain any free zirconia at that stage, as found by X-ray diffraction. However, when these are sintered at higher temperatures, free zirconia begins to appear. The fact that the Hong Na-zirpsios at $x = 2.1$ and 2.2 sintered at 1398 K do not contain any free zirconia confirms the existence of the Hong solid solution even at high x values. The formation of zirconia in the system hence has to be attributed to the decomposition of the material at higher sintering temperatures. In addition to the formation of free zirconia they also form a glassy phase. This glassy phase is common to both the Hong and the Max Planck type materials, although free zirconia is never present in the latter. It is speculated that the glassy phase is produced as a result of the sintering mechanism.

An examination of the sintering curves reveals that the density of the sinter increases to the maximum within a very narrow range of temperature of about 30 K. Also, the sintering rates are extremely fast - samples can be nearly fully sintered in 15 min at the optimum temperatures. These facts suggest that a liquid phase mechanism is involved in the sintering of these materials. Because the Na-zirpsios are solid solutions, at the beginning of the melting of the material the liquid that is formed will have the composition represented on the liquidus curve while the composition of the solid moves up on the solidus curve. On cooling rapidly, as it is done in normal sintering practice, the liquid phase produces a glass instead of crystallizing into the original Na-zirpsio. This model of the sintering mechanism assumes that the original precursor prior to sintering is glass-free. It has been found that the X-ray patterns of Na-zirpsios synthesized at about 1173 K are quite sharp with very low background. On the other hand, after heating these to about 1473 K the patterns reveal increased background levels. It is thus reasonable to assume that the Na-zirpsio precursor powder is at least relatively glass-free at the lower temperatures. If that is the case, it is difficult to visualize a Na-zirpsio product free of glass in a sintered form.

The hot-pressing technique for fabrication of the Na-zirpsio was utilized with a view to reducing the sintering temperature and hence the possibility of glass formation. However, even the hot-pressing procedure did not apparently eliminate the liquid phase densification mechanism. X-ray patterns of the hot-pressed specimens also showed relatively high background levels, thereby implying the presence of non-crystalline phases.

In addition to the X-ray diffraction analysis, the microstructural analysis by SEM also reveals the glassy phase when the thickness of the glass layer matrix is large enough. An EDAX spot analysis (semiquantitative) indicated that the glassy phase had a considerably different composition than the crystalline phases. The glassy phase always contained less zirconia. This may mean that even the initial melting of the Na-zirpsio precursor may not be producing a liquid phase whose composition is on the solid solution liquidus line. A fully melted Max Planck type material at x = 2 yielded free zirconia, a crystalline phase, which was a sodium zirconium silicophosphate, and a glassy phase that had a zirconia deficient Na-zirpsio composition. The phase diagram of the four component soda-zirconia-silica-phosphorus pentoxide system is required for a full understanding of the Na-zirpsio synthesis and sintering.

The Stability of Na-zirpsios in Water

Earlier work in this laboratory (6) has shown that Na-zirpsios containing alumina as an impurity react with water much faster than those without the impurity. There was an increase in the glass content of the system when the alumina impurity was present. In the present investigation it has been found that the compositions with high x values contain more glass than in the low x materials. The reaction rate of the high x Na-zirpsios with water is again much faster than with low x products. These facts suggest that the glassy phase present in the sintered and hot-pressed Na-zirpsios may be responsible for their deterioration in water.

Although all the Na-zirpsio compositions react with water to varying degrees, the compositions with the lowest x values have the greatest stability. At x = 1.5, the pH rises to only about 6 even after prolonged exposure to water. The increase in alkali concentration required for such a change is practically negligible. Hence, if the Na-zirpsios with low x values have sufficiently large ionic conductivities, they may be practically useful for

the applications envisaged, on a water reactivity basis. These materials could possibly also be used for the electrolytic preparation of their hydrogen conducting forms. However, because one of the major projected applications is in high energy efficiency storage batteries employing molten sodium and sulphur, the stability of these materials in contact with the latter elements must be properly ascertained before such compositions are tested in battery applications. Some of these tests are in progress at our laboratory at the present time.

CONCLUSIONS

Using the gel-processing technique developed at CANMET, both Hong and Max Planck type Na-zirpsios can be synthesized at temperatures in the order of 1273 K. Dense sintering requires higher temperatures and these depend on the composition and Na-zirpsio type. The sintering temperature increases with an increase in the x value in the Max Planck material but decreases in the case of the Hong compositions where $1.5 < x < 2.2$.

Hot pressing of Na-zirpsios produces high density samples at 50 - 225 K lower than that required for the conventional sintering.

The sintering kinetics indicate that a liquid phase mechanism is involved in the process, which produces a glassy phase in the final product.

All the Na-zirpsio products prepared in the present investigation react with water. The rate and extent of this reaction increase with an increase of x in the sample. It is speculated that the glassy phase present in the sintered Na-zirpsios is responsible for their deterioration in water.

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Table 1 - General formulae of the compositions studied in present work

Name	Composition	Reported by
Na-zirpsio (Hong)	$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$	Hong (1)
Na-zirpsio (Max Planck)	$Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-2x/3}$ where $1.5 < x < 2.2$	von Alpen (3)

Table 2 - Specific compositions of the Na-zirpsios prepared

	Composition	
x	Hong type	Max Planck type
1.5	$Na_{2.5}Zr_2Si_{1.5}P_{1.5}O_{12}$	$Na_{1.5}Zr_{1.50}Si_{1.5}P_{1.5}O_{11.00}$
1.8	$Na_{2.8}Zr_2Si_{1.8}P_{1.2}O_{12}$	$Na_{2.8}Zr_{1.40}Si_{1.8}P_{1.2}O_{10.80}$
1.9	$Na_{2.9}Zr_2Si_{1.9}P_{1.1}O_{12}$	$Na_{2.9}Zr_{1.37}Si_{1.9}P_{1.1}O_{10.73}$
2.0	$Na_{3.0}Zr_2Si_{2.0}P_{1.0}O_{12}$	$Na_{3.0}Zr_{1.33}Si_{2.0}P_{1.0}O_{10.67}$
2.1	$Na_{3.1}Zr_2Si_{2.1}P_{0.9}O_{12}$	$Na_{3.1}Zr_{1.30}Si_{2.1}P_{0.9}O_{10.60}$
2.2	$Na_{3.2}Zr_2Si_{2.2}P_{0.8}O_{12}$	$Na_{3.2}Zr_{1.27}Si_{2.2}P_{0.8}O_{10.53}$

Table 3 - Optimum calcination and sintering temperatures used for the various compositions

Composition (x)	Temperature, K		
	Calcining	Sintering	Hot-pressing
A. Hong type:			
1.5	1023	1573	1523
1.8	1023	1548	1498
1.9	1023	1548	1498
2.0	1023	1498	1298
2.1	1123	1398	1223
2.2	1123	1398	1223
B. Max Planck type:			
1.5	1148	1398	1348
1.8	1148	1448	1348
1.9	1023	1448	1348
2.0	1023	1448	1348
2.1	1223	1598	1398
2.2	1223	1598	1373

Table 4 - Linear rate constants for the reaction of Na-zirpsios with water at 298, 303 and 308 K

Composition (x)	Linear Rate Constant, K_1, mol/cm^2-min at 298K	303K	308K
A. Hong type sintered:			
1.5	0.59E-11	0.99E-11	1.91E-11
1.8	2.23E-11	7.56E-11	6.89E-11
2.0	0.44E-11	0.58E-11	1.57E-11
2.1	1.16E-11	3.24E-11	3.30E-11
2.2	1.91E-06	1.47E-06	0.72E-06
B. Hong type hot pressed:			
1.5	0.39E-10	0.75E-10	1.86E-10
2.0	2.14E-11	2.81E-11	7.05E-11
2.1	6.72E-09	5.97E-09	3.85E-09
2.2	1.18E-07	1.17E-07	0.46E-07
C. Max Planck sintered:			
1.5	0.79E-11	1.01E-11	2.31E-11
1.8	2.14E-07	0.53E-07	1.74E-07
1.9	0.14E-10	1.35E-10	5.16E-10
2.0	0.51E-10	1.09E-10	0.76E-10
2.1	1.06E-06	1.30E-06	1.17E-06
2.2	1.37E-07	5.00E-07	5.98E-07
D. Max Planck hot pressed:			
1.5	1.36E-11	1.71E-11	2.18E-11
1.8	1.70E-11	4.98E-11	8.67E-11
1.9	0.33E-09	0.50E-09	8.90E-09
2.0	2.47E-08	4.15E-08	3.95E-08
2.1	9.27E-07	5.40E-07	4.84E-07
2.2	3.67E-07	3.96E-07	6.48E-07

Table 5 - Activation energies for the reaction between Na-zirpsios and water

	Composition (x)	Activation energy kcal/mol
A. Hong type, sintered:		
	1.5	21.37
	1.8	16.50
	2.0	22.99
	2.1	19.22
	2.2	-17.77
B. Hong type, hot pressed:		
	1.5	28.54
	2.0	21.67
	2.1	-10.15
	2.2	-17.30
C. Max Planck, sintered:		
	1.5	19.39
	1.8	-3.90
	1.9	65.69
	2.0	7.56
	2.1	1.78
	2.2	26.98
D. Max Planck, hot pressed:		
	1.5	8.70
	1.8	29.81
	1.9	59.75
	2.0	8.61
	2.1	-11.90
	2.2	10.34

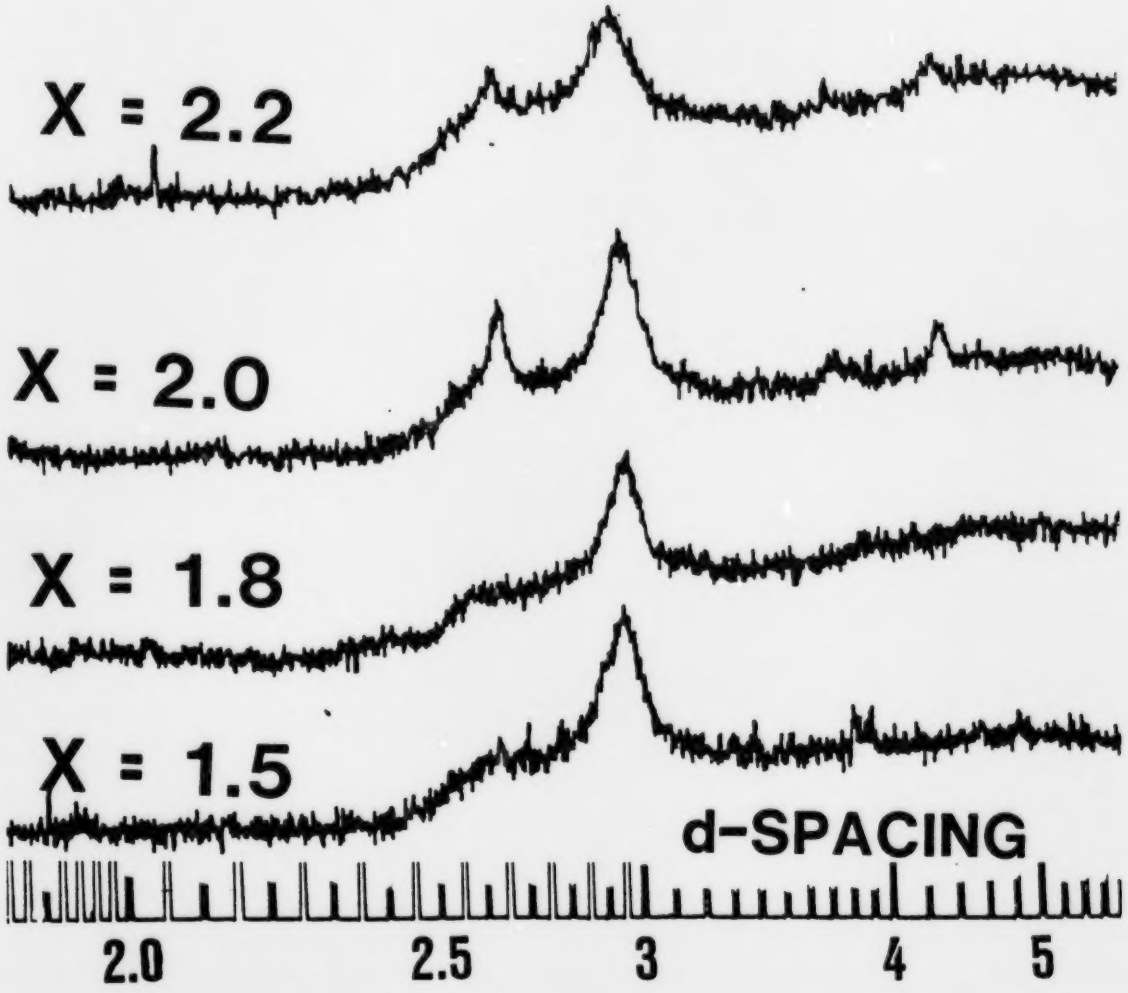


Fig. 1 - X-ray diffraction pattern (Guinier) of Na-zirpsio precursor powders calcined at 973 K

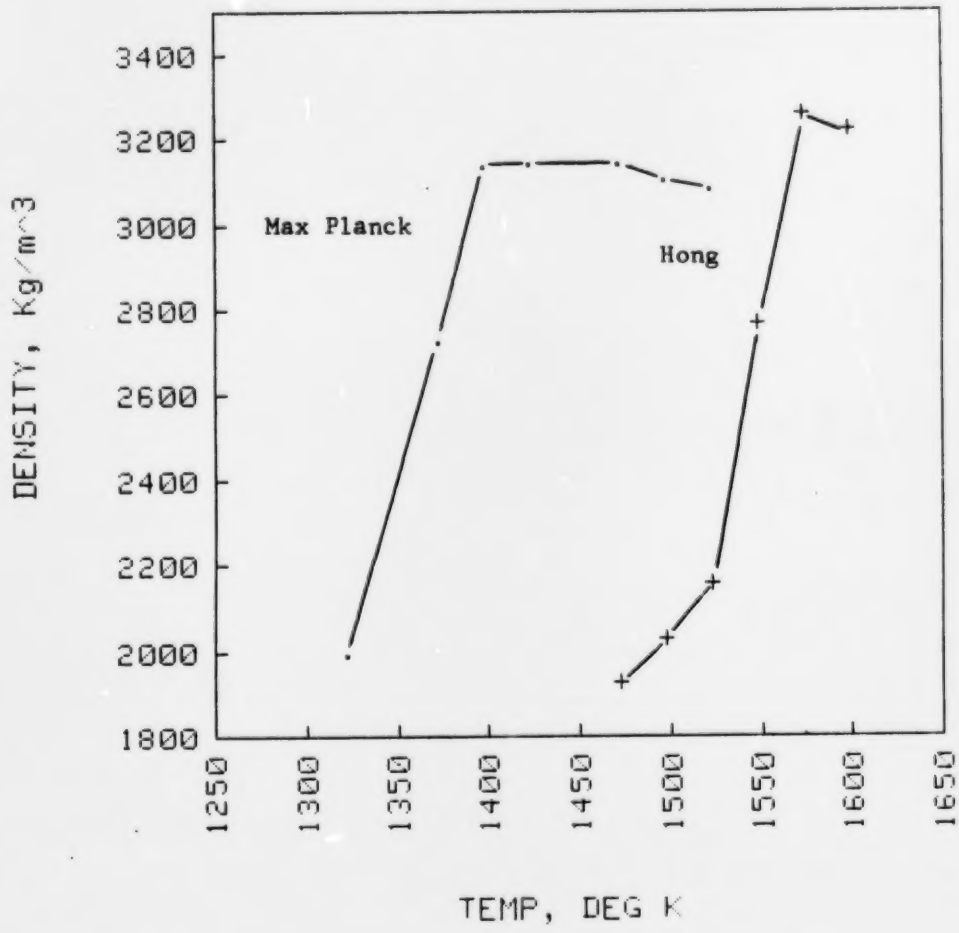


Fig. 2 - Sintering curves showing the effect of temperature on the densification of Hong and Max Planck Na-zirpsio at x = 1.5

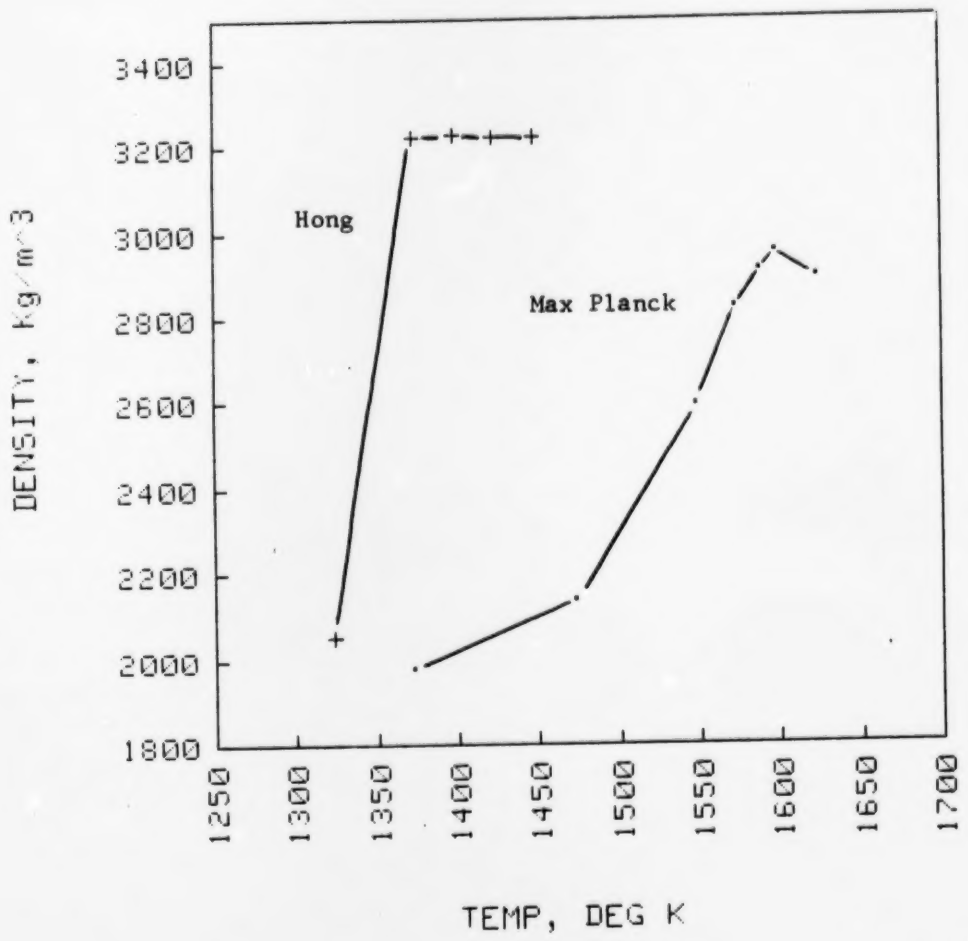


Fig. 3 - Sintering curves showing the effect of temperature on the densification of Hong and Max Planck Na-zirpsio at x = 2.2

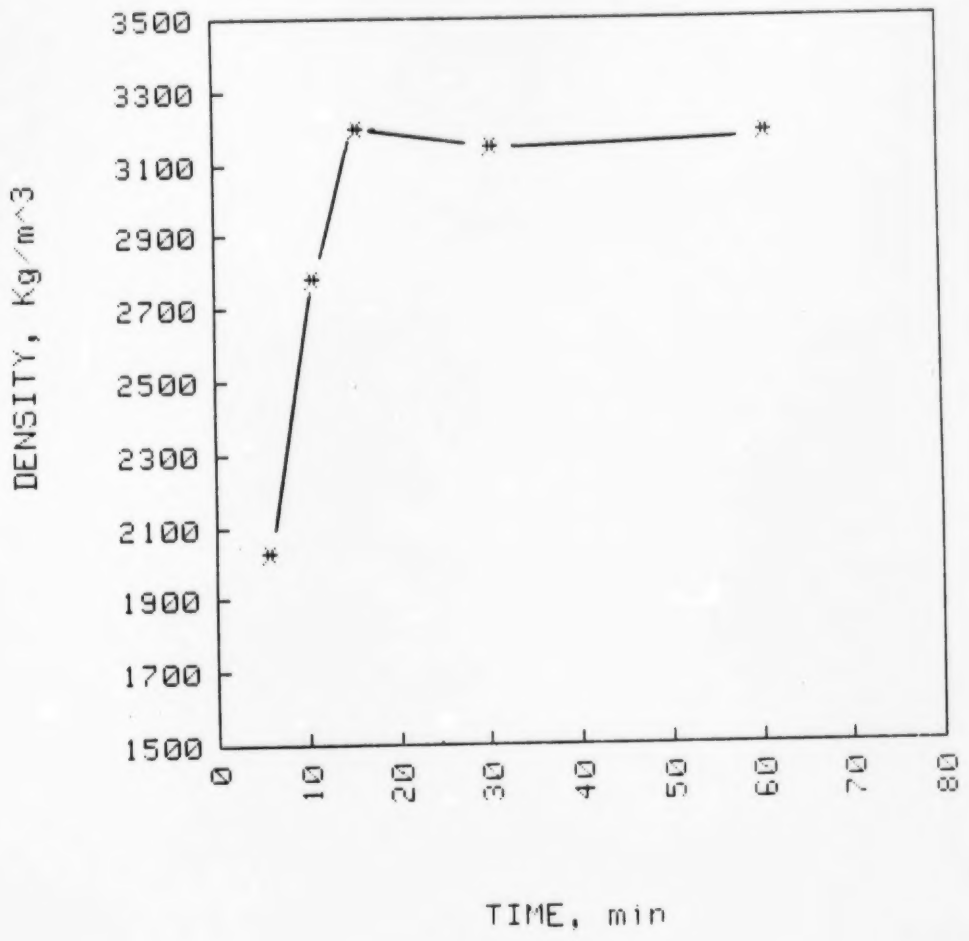


Fig. 4 - The effect of time on the sintering of Na-zirpsio at 1448 K. The composition is Max Planck x = 1.8

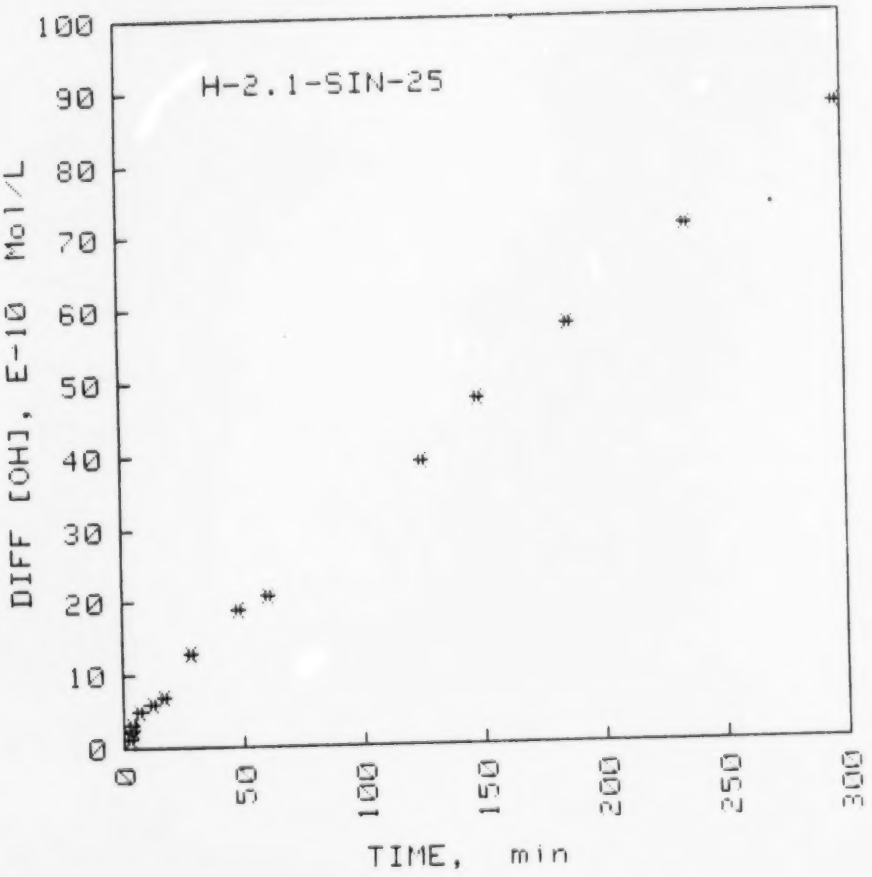


Fig. 5 - Plot showing the linear kinetic behaviour of Na-zirpsio-water reaction

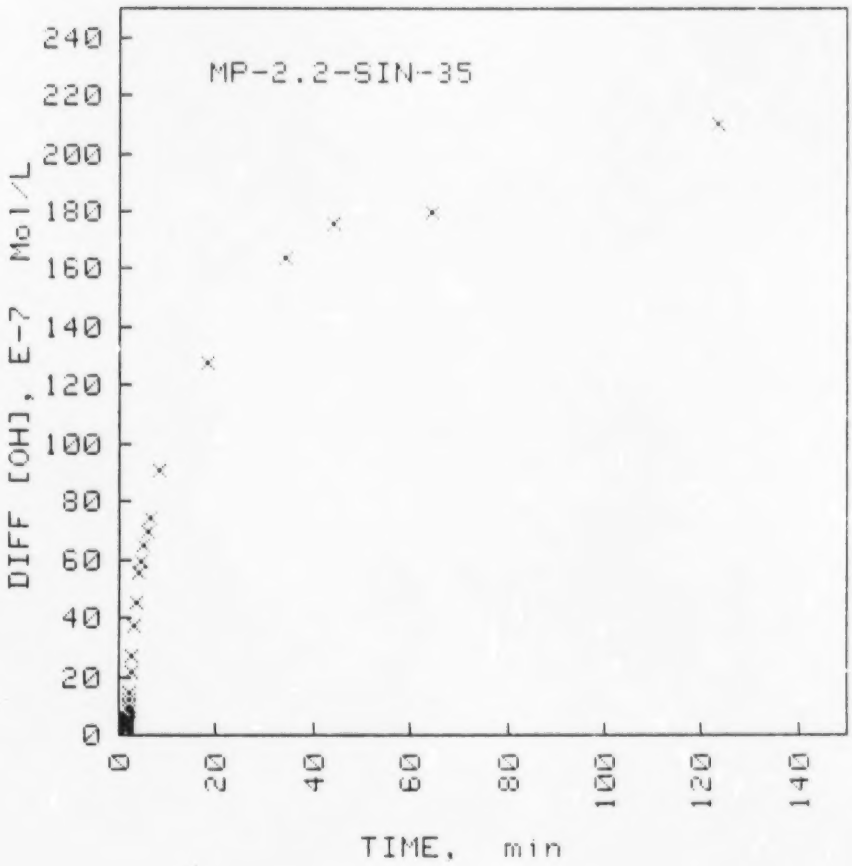


Fig. 6 - Linear-parabolic rate behaviour of certain Na-zirpsio-water reactions

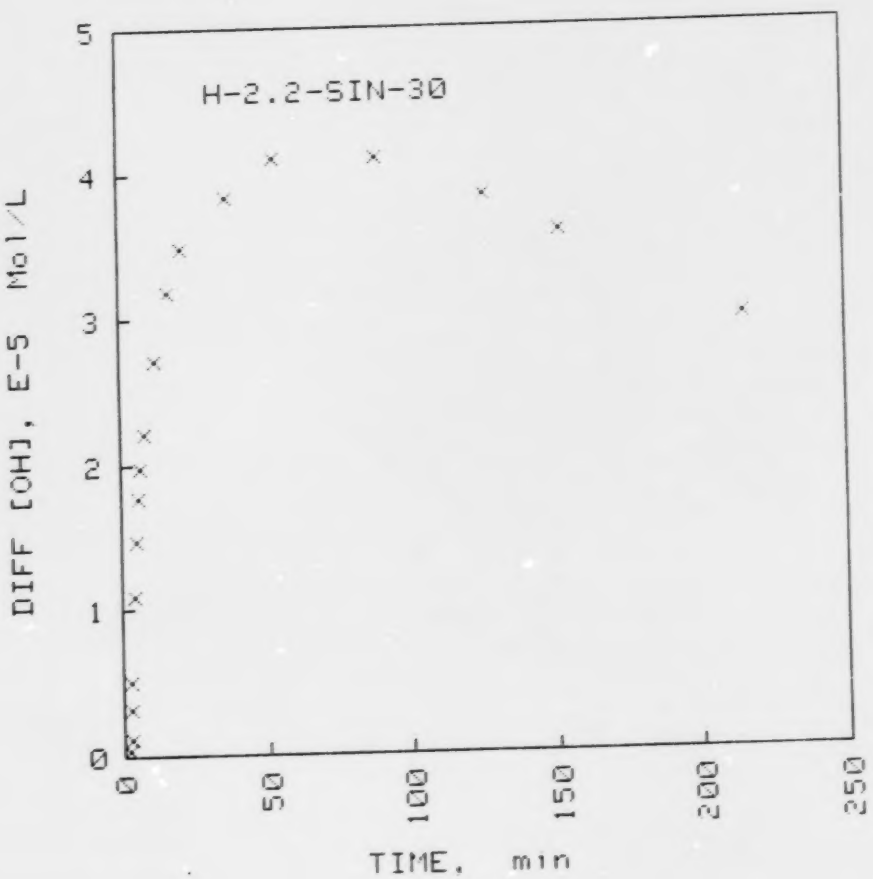
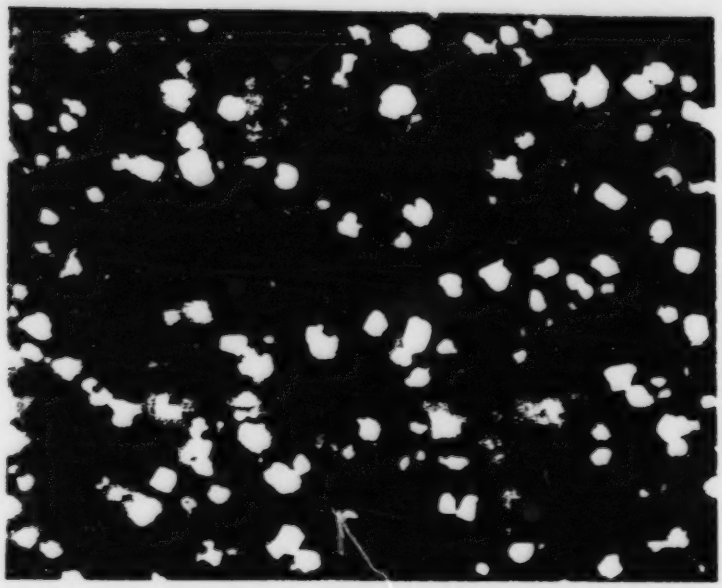
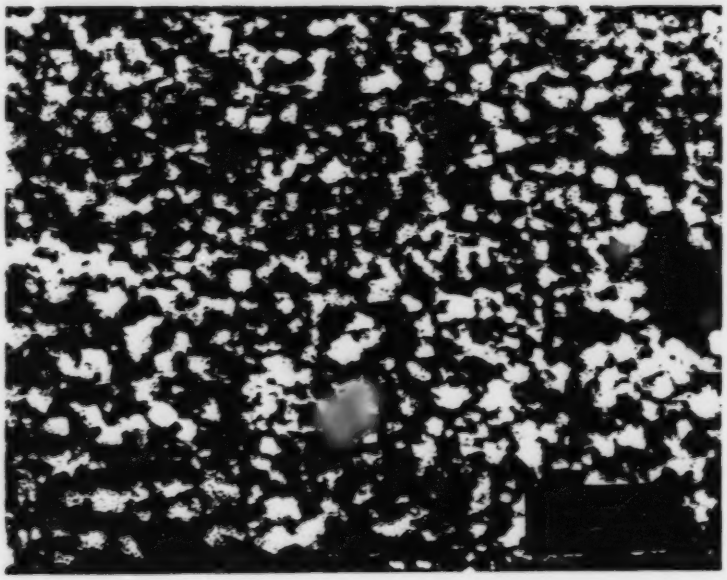


Fig. 7 - Plot of kinetics of certain Na-zirpsio-water reactions showing a maximum in the hydroxyl ion concentration



(a)



(b)

Fig. 8 - SEM of polished sections of sintered Na-zirpsios at x = 1.8:

(a) Hong-type showing zirconia, light; Na-zirpsio, light grey; glassy phases, dark grey

(b) Max Planck-type showing Na-zirpsio, light grey; glassy phases, dark grey

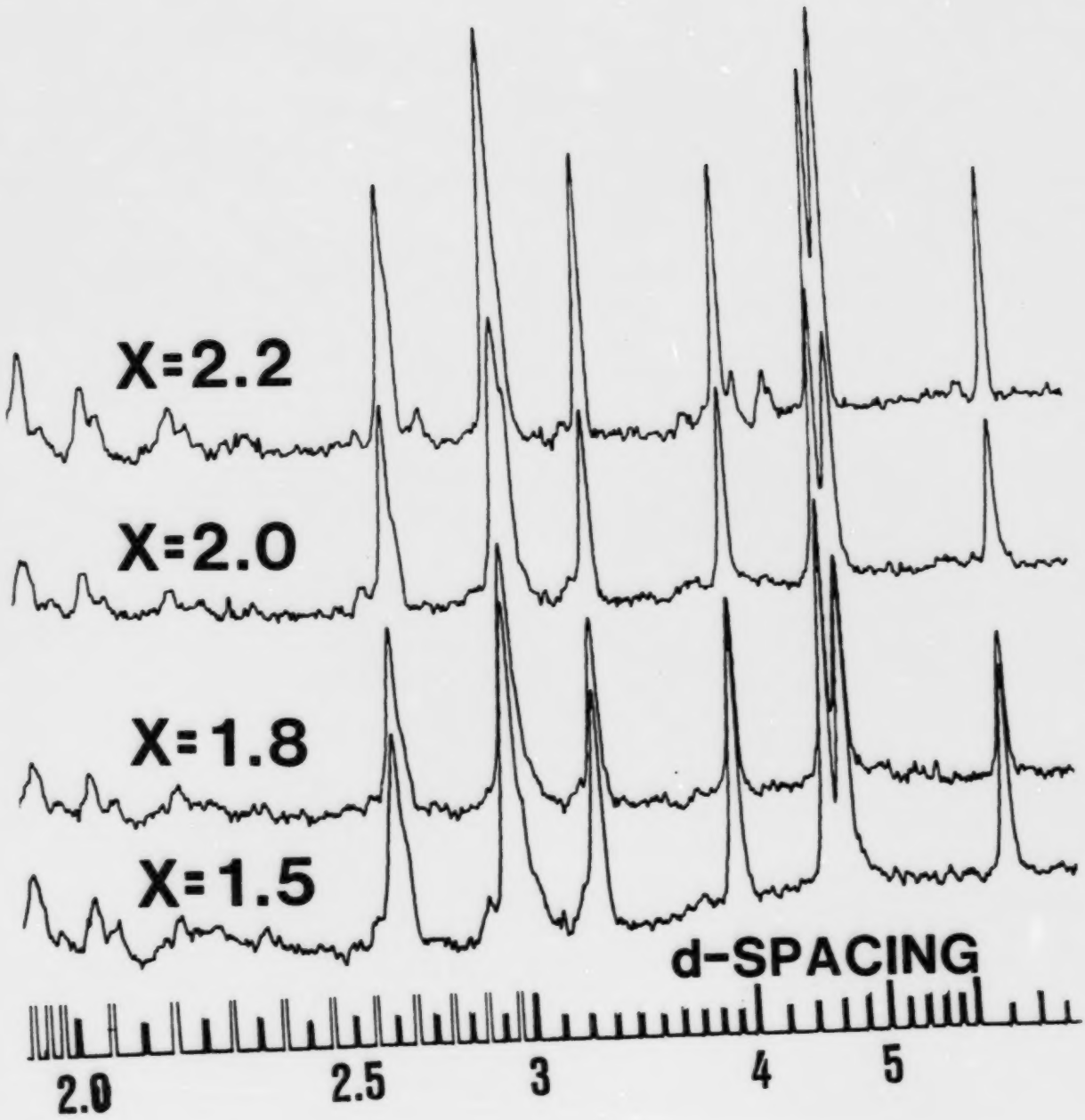


Fig. 9 - X-ray diffraction patterns (Guinier) of various Na-zirpsio compositions (Hong) after calcination at 1273 K. Patterns are sharp and no monoclinic zirconia is evident.